APPROXIMATE CALCULATION OF THE SURFACE TENSION OF METALS

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WASHINGTON, D.C. 20546   MARCH, 1968

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ABSTRACT: *A method is developed for calcu-
lating surface tension in metals on the ba-
sis of their heats of vaporization, using a
polar model of a metal. A table is given which
lists surface tension values for eleven metals
and compares the author's results with data
from the literature.*

In our opinion, the principle shortcoming of the available
calculations of the surface tension of metals [1-7] is the fact
that the number of free electrons Z per atom of metal entering
into the formulas obtained theoretically, is chosen arbitrarily to
a certain degree by the authors. One of them uses the maximum
valency of the atom for Z; a second uses the average value of the
chemical valence; a third uses a figure of one free electron per
atom of metal, etc. However, such an important characteristic
of metal as the Z number must be determined primarily on the basis
of experiments, as was pointed out with complete justification
in [8].

In addition, the majority of calculations of σ do not give
the temperature dependence of the surface tension of metals, since
the calculations of σ are based on a temperature of absolute zero.
The problem   of the temperature dependence of σ in metals is dis-
cussed in [9-11].

It seems to us that it would be desirable to formulate a the-
ory of surface tension of metals whose definitive formulas for σ
would   include other physical constants of metals which would be
readily available to experimental determination.

At various times, a number of authors have suggested empir-
ical and semi-empirical formulas for calculating the σ of metals
in terms of the work function of the electron in leaving the metal
[12, 13], the heat of vaporization [14], etc. The values of σ cal-
culated by these formulas show a better agreement with experimen-
tal data than with the data obtained by theoretical formulas.

In the present paper, we wish to present an approximate cal-

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* Numbers in the margin indicate pagination in the foreign text.

culation of σ for metals in terms of their heat of vaporization.

We shall begin with the following variation of the polar model of a metal. Let us consider a metal in the solid state at temperature T. We will assume that the average values of the coordinates of the positive ions of the metal coincide with the lattice points of the crystal lattice, while the average values of the coordinates of the free electrons are distributed symmetrically within the crystal lattice so that an "electron lattice" is formed having exactly the same structure as the lattice of positive ions, except that it is displaced relative to the latter. The volume unit cells and basal planes of the metal lattice must be neutral.

Consequently, in the polar model under consideration, we will have a coordination ion-electron lattice of a metal, which, e.g., in the case of a metallic face-centered cubic lattice, will have a cubic shape of NaCl type, with a minimum distance between the cation and the "anion" $a/2$, where a is the period of the metal lattice.

In [11] we gave the following formula for the coefficient of the surface tension of metals:

$$\sigma = -n_s \frac{\Delta f}{f_{k v}} [3kT \ln 2 - 2(E_0' - E_0)].$$ (1)

where (for the polar model of a metal which we have assumed) f_{hv} is /454 the coordination number of the cation relative to the "anion"; Δf is the number of insufficiently close "anions" in the cation at the surface of the metal; E_0 and E_0' are the free energies at $T = 0$, which a particle within the metal would have, if its mean vibrational frequencies were equal to ν and $\nu/\sqrt{2}$, respectively, and the coordination numbers were equal to f_{kv} and $f_{hv}/2$, respectively. We shall calculate the values E_0 and E_0' as follows. Since E_0 is the energy required for dividing a metal into free ions and free electrons at $T = 0$, if we impart this energy to the metals at the beginning, than the energy $\sum_{i=1}^{z} eV_i$, where V_1, V_2... represent the first, second, etc., ionization potentials of the atom, and finally, assuming a heat of sublimation at absolute zero of L_0, we will obtain the original state of the metal. From this it follows that

$$|E_0| = \sum_{i=1}^{z} eV_i + L_0,$$ (2)

$$|E_0'| = \sum_{i=1}^{z} eV_i + L_0'.$$ (3)

Substituting (2) and (3) into (1) and assuming (as in [11]) that the free energy is a linear function of f_{hv}, we obtain

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$$\sigma = -n_s \frac{\Delta f}{f_{kv}} [3kT \ln 2 - L_0]. \tag{4}$$

Formula (4) makes it possible to obtain the value of σ for various faces of an ideal single crystal at the temperature T.

Ya. I. Frenkel' [15] showed that the surface of a crystal in the equilibrium state exhibits roughness owing to the temperature fluctuations. We will therefore assume that only short-range order is retained on the surface of the crystal, corresponding to the orientations of all the basal faces of the elementary electron-ion lattice. In this case, the surface tension of the crystal will be

$$\sigma = -\bar{n}_s \frac{\overline{\Delta f}}{f_{kv}} [3kT \ln 2 - L_0], \tag{5}$$

where $\bar{n}_s$ is the average number of particles per unit surface; $\overline{\Delta f}/f_{kv}$ is the average value relative to the number of deficient neighbors ("anions") in a positive ion of the metal at the surface. The values of $\bar{n}_s$ and $\overline{\Delta f}/f_{kv}$ are determined as follows. Let us consider any positive ion of the metal and compare the probability w'' of its location per unit area on the surface of a metal with a probability w' of its existence per unit area of any plane parallel to the surface and passing through the metal; we will obtain

$$w''/w' = e^{-\overline{W}_i/kT}, \tag{6}$$

where W_i is the work required for the ion to move from the inside to the surface, proportional to the number of deficient neighbors Δf_i at the surface. On the other hand, the ratio of their probabilities w''/w' must be equated to the ratio of the number of ions $n_i^{(s)}$ per unit area on the surface of the metal to the number of ions $n_o^{(s)}$ per unit area within the metal. Therefore, from (6) we have

$$n_i^{(s)} = n_0^{(s)} e^{-W_i/kT}. \tag{7}$$

Therefore, on the surface of the metal we have $n_i^{(s)}$ particles per cm^2, with an excess energy W_i and consequently adjacent to the i-th face of the cubic crystal, we have

$$\sum_i \frac{n_i^{(s)}}{f_i^{(s)}} S_i = 1, \tag{8}$$

where S_i is the area of the i-th face; $f_i^{(s)}$ is the number of ions /455 per elementary lattice of the basal lattice for this face. From (7) we obtain

$$\bar{n}_s = n_0^{(s)} \sum_i x_i, \tag{9}$$

where $x_i = \exp\left[-\dfrac{\alpha \Delta f_i}{kT}\right]$ (Δf_i is the number of deficient neighbors for the i-th face).

The average value relative to the number of deficient neighbors at the surface of the metal will be

$$\frac{\overline{\Delta f}}{f_{kv}} = \frac{\sum_i \dfrac{\Delta f_i}{f_{kv}} x_i}{\sum_i x_i}. \tag{10}$$

We know that in a crystal with a cubic system, there are 6 (100) faces, 12 (110) faces, and 8 (111) faces, for which the number of deficient neighbors is equal to 1, 2, and 3, respectively, when these faces are located at the surface of a metal. For each of these faces, $f^{(s)} = 2$. Consequently, if we take (7) into consideration and also the fact that $S_{(100)} = a^2$, $S_{(110)} = a^2 \sqrt{2}$ and $S_{(111)} = a^2 \sqrt{3/2}$, we can write Expression (8) as follows:

$$\frac{n_0^{(s)}}{n_{(100)}^{(s)}}\left(6 x_{(100)} + 12\sqrt{2}\, x_{(100)}^2 + 8\frac{\sqrt{3}}{2}\, x_{(100)}^3\right) = 1, \tag{11}$$

where $x_{(100)} = \exp - \dfrac{\alpha \Delta f_{(100)}}{kT}$ ($\Delta f_{(100)}$ is the number of deficient neighbors for the (100) face); $n_{(100)}^{(s)}$ is the number of particles per cm^2 of the (100) face. Let us continue the calculation for a surface which is parallel to the (100) face inside the crystal. Taking $n_0^{(s)} = n_{(100)}^{(s)}$, we find from (11) the value $x_{(100)}$, which satisfies the condition $0 \le x_{(100)} \le 1$, $x_{(100)} = 0.122$. From (9) and (10), we obtain $\bar{n}_s = 0.924\, n_{(100)}^{(s)}$ and $\overline{\Delta f}/f_{kv} = 0.201$. By differentiating Equation (5) for temperature and disregarding the temperature dependence $\overline{\Delta f}/f_{kv}$, we find the value of the temperature coefficient γ for the surface tension of metals:

$$\gamma \equiv \frac{d\sigma}{dT} = -\left(3k\frac{\overline{\Delta f}}{f_{kv}}\bar{n}_s \ln 2 + 2\alpha\sigma\right), \tag{12}$$

where α is the temperature coefficient of the linear expansion of the metal. The results of calculating the surface tension according to Formula (5) and the temperature dependence according to Formula (12) for metals with a face-centered cubic system are given in Table 1. The same table gives experimental values of σ and γ for alloyed metals, the scatter of the experimental data

according to the measurements of various authors, the most reliable values of σ according to the analysis of the experimental data in [16], and the results of the most recent measurements. In all

TABLE 1

metal	$n^{(s)}_{100} \cdot 10^{14}$	$L_s \cdot 10^{12}$ elec/atom	T-pa, °K	σ, elec/cm^{-2}		γ, elec·cm^{-2}·deg^{-1}	
				calc	exp	calc	exp
Ag	11,1	4,70[20]	1268	898	751—940 923[16]	—0,123	—0,13[16]
Au	110,0	5,76	1473	1100	581—1420 1120[16]	—0,092	—0,10[16]
Cu	14,6	5,27	1473	1380	1103—1400 1154[16]	—0,204	—
Pb	7,62	3,50	600	470	424—536 461[16]	—0,078	—(0,06—0,25)[16]
Al	11,5	4,15	973	832	520—914 860[18]	—0,103	—(0,135—0,35)[19]
Pt	12,0	8,75	2273	1815	1819[16]	—0,097	—0,1
γ-Fe	14,0	7,43	1843	1970	950—1210 1720[21]	—0,12	—
Ca	6,61	2,71	1123	298	320	—0,048	—
β-Co	16,0	8,3	1763	2320	—	—0,142	—
β-Ni	16,2	6,97	1725	1957	1735[19]	—0,132	—
β-Tl	8,50	3,03	573	454	436—485[16]	—0,086	—

cases where it was possible, we determined σ_{exp} on the basis of measurements in a vacuum. As the experimental values of the heat of sublimation, we used the data calculated by Rabinowitsch and Thilo [17], at a temperature of absolute zero, as well as the data for Ag from [20].

It is clear from Table 1 that the calculated values of σ and γ , regardless of the roughness of the model of the metal used and the approximate nature of all the calculations, are in good agreement with the most reliable experimental data, especially for Pb, for which the experimental value of σ is known with special accuracy. In the majority of the remaining cases, the difference between σ_{calc} and σ_{exp} does not exceed 5%; it is only in the cases of Cu, γ-Fe, and β-N that it is roughly equal to 10-20%.

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